

AD-A159 759 RADIATIVE LIFETIMES AND KINETIC STUDIES OF METASTABLE NO(+) (A 3 SIGMA(+)) AND O2(+) (A 4 PI SUB U)(U) NAVAL RESEARCH LAB WASHINGTON DC A O'KEEFE ET AL. 1985 1/1
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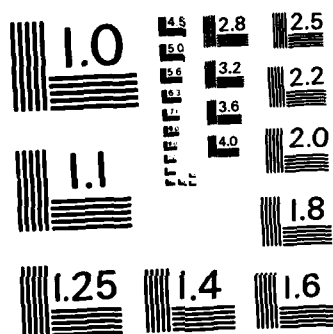
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AD-A159 759

Radiative Lifetimes and Kinetic Studies of
Metastable $\text{NO}^+(\text{a}^3\Sigma^+)$ and $\text{O}_2^+(\text{a}^4\Pi_u)$

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Abstract

The lowest energy metastable electronic states of the nitric oxide and molecular oxygen cations have been studied using Fourier Transform Mass Spectrometry. Using very low neutral reactant pressures and ion trapping periods of up to several seconds, the radiative relaxation rate of the metastable ion becomes competitive with its reaction rate. In this fashion both kinetic information and the radiative lifetime of the metastable state are obtained. The measured rate constants for the reactions of $\text{NO}^+(\text{a}^3\Sigma^+)$ with CO_2 ($k = 1.0 \pm 0.2 \times 10^{-9} \text{ cm}^3/\text{sec}$) and of $\text{O}_2^+(\text{a}^4\Pi_u)$ with Ar ($k = 4.9 \pm 1.5 \times 10^{-10} \text{ cm}^3/\text{sec}$) are in agreement with earlier results. The measured lifetimes of the NO^+ metastable ($\tau = 1.45 \text{ sec}$) and the O_2^+ metastable ($\tau = 0.22 \text{ sec}$) are discussed using a four state spin-orbit coupling model which predicts metastable radiative lifetimes which agree reasonably well with the experimental values.

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INTRODUCTION

In most studies of ion-molecule reactions one of the underlying assumptions is that the reactant ions are produced in, or are quickly relaxed into and react from their ground electronic and vibrational states. Since direct spectroscopic confirmation of this assumption is usually not feasible, justification for such assumptions relies upon the use of gentle ionization techniques or thermalizing bath gasses¹⁻². While this assumption is undoubtedly justified in many cases, several exceptions have been found where excited states populations persist for long times allowing kinetic studies of these species³⁻⁵. In these cases it has been found that the chemistry of the excited state is, not surprisingly, different from that of the relaxed ground state. Of particular interest from a chemical standpoint are ionic excited states which are metastable by virtue of a spin difference with the ground state. These states will, for small ions composed of light atoms, live for substantial time periods, and will generally correlate with different reaction projects from those of the ground state ionic reactant. Such spin metastables would be expected to be of importance in the chemistry of metal ions and metal cluster ions since these species are typically generated by rather violent processes⁶⁻⁸.

In the present study we examine the lowest metastable electronic states of the NO^+ and O_2^+ ions. Using long storage times within an Ion Cyclotron Resonance (ICR) cell, the lifetimes of these metastable states are probed using the technique of competitive reactions. These are important test systems since



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after formation by electron impact (see the Appendix) the fraction of $(\text{NO}^+(\text{a}^3\Sigma^+))/(\text{NO}^+(\text{total}))$ in the cell to be $f \approx 0.66$.

If this state is long lived, it may play an important chemical role in environments where such ionization occurs.

The O_2^+ ion is better characterized spectroscopically⁹ with much of the recent work focusing on the metastable quartet states¹⁵⁻²¹. Electronic potential energy curves from Krupenie²² are shown in Fig. 2. It is estimated (see the Appendix) that, in this case too, a significant fraction ($f \approx 0.5$) of the ions formed by electron impact or other Franck Condon processes will be in the metastable quartet manifold of states. Some ion-molecule reactions involving $\text{O}_2^+(\text{a}^4\Pi_u)$ have been studied by Lindinger, et al.³, demonstrating that metastable O_2^+ is, like metastable NO^+ , much more reactive than the ground state ion.

The forbidden optical transitions of the lowest metastable states of NO^+ and O_2^+ to the respective ground electronic states have never been spectroscopically observed. The long ion storage times possible with an ICR ion trap permit the determination of radiative lifetimes of these states which would be difficult to measure by direct, photon collection. In addition to the determination of excited state radiative lifetimes, these studies provide complimentary chemical kinetic information about the metastable states.

In this study we exploit the difference in chemical reactivity of the ion ground and metastable electronic states, using it to probe the ion population which is stored in the ICR cell. If we monitor the rate at which the metastable ion population is

depleted due to reaction with an added neutral we can control conditions so as to measure pseudo-first-order kinetics. The disappearance rate for the metastable ion is the sum of the reaction rate, the electronic quenching rate, and the radiative decay rate. Plotting the observed disappearance rate as a function of neutral reactant concentration yields a zero neutral reactant concentration intercept equal to the radiative decay rate. In addition, the slope of the second order plot, assuming negligible electronic quenching, yields the reaction rate constant. These measurements are compared with independent determinations obtained by other means.

EXPERIMENTAL

Studies were performed with a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTMS) using a 1 inch cubic trapping cell positioned between the pole faces of a 0.9 T electromagnet. The system is operated under high vacuum (base pressure $< 5 \times 10^{-9}$ Torr) conditions. The experiments were controlled by a Nicolet FTMS-1000 Data handling system. The theory, instrumentation, and methodology of FTMS and ion cyclotron resonance have been described in detail elsewhere²³⁻²⁵, have only a brief description of pertinent details of the technique will be given here.

A schematic representation of the sequence of events involved in these studies is shown in Fig. 3. Positive ions are formed within the ICR cell by electron impact of 70 eV electrons. The electron gun is mounted on the side of the cubic cell; the

current at the cell is pulsed by switching a grid voltage between the filament and the cell. The electrons are directed through the cell parallel to the applied magnetic field for a the period of 10-20 msec. Ions formed within the cell undergo cyclotron motion due to the presence of the magnetic field; the cyclotron frequencies are proportional to magnetic field strength, B , and inversely to the ion mass. Ion motion along the magnetic field axis is restricted by the application of a positive electrical potential to the cell walls which are perpendicular to the magnetic field. This potential is maintained high enough (Trapping voltage = 3 volts) to prohibit the loss of ions which may be formed by chemical reactions with excess kinetic energy.²⁶⁻²⁷ Since electron impact ionization at 70eV is expected to produce ions in a number of excited electronic states the ionization period is followed by relaxation period of 100 msec for NO^+ and 50 msec and O_2^+ . During this period radiative relaxation occurs which results in a funneling of population into the ground and lowest metastable levels of the ions.

Following the relaxation period ions other than the prepared reactant ion are removed from the ICR cell by means of swept frequency ejection. In this process kinetic energy is coupled into the ion through the application of an a.c. voltage signal to cell plates perpendicular to the plane of ion cyclotron motion. When the two frequencies match, the ion absorbs energy, increasing its orbit radius until it collides with a cell wall and is removed. In practice, the operating system sweeps through a predetermined range of frequencies corresponding to a range of

ion masses (or, more accurately, a range of mass/charge values). In this fashion the cell is cleared of interfering ions and contains only the prepared reactant ion, which may still be present in a mixture electronic states. The stored ions are then allowed to react with the added neutral gas for a fixed time period, the reactant time is varied over a range wide enough to generate a reactant disappearance curve.

Detection of the ions is based upon a two-step process in which first, the ions are kinetically excited using a swept frequency excitation and then, the image current appearing in the cell plates as a result of the synchronous ion motion is monitored. This measured image current is the superposition of frequencies corresponding to the trapped ion cyclotron frequencies. When the Fourier Transform of this signal is taken, the result is a population vs. frequency spectrum. If the magnetic field is accurately known, the frequency spectrum may be transformed into a conventional mass spectrum. More detailed discussions of the principles of FTMS are given by Comisarow and Marshall²⁸ and others.^{23,24,29}

The advantages of this technique over the conventional ICR approach are several. In addition to the increase in mass resolution offered by FTMS the benefits include a much increased data collection rate resulting in part from the fact that an entire mass spectrum may be collected at one time. These factors are of great importance in the present study since slow drift in

experimental conditions would have made accurate determination of ion signal intensities difficult or impossible at the long trapping times required.

Since the observed peak width does not vary with peak height, the relative populations of product and reactant ions are determined by peak heights. Peak heights also vary linearly with added gas pressure as measured by a Bayard-Alpert type ionization gauge. The response of the ionization gauge was calibrated by comparison of the measured and known rate constants for the charge transfer reaction of N_2^+ with CO_2 .

Since the reactant ion is prepared in a mixture of two electronic spin states (see Appendix), only one of which is reactive, only a partial decline in reactant ion signal will be observed - even at high neutral reactant concentrations. Consider a situation where we form a mixture of ground and excited state reactant ions, A^+ and A^{*+} , in which only the higher energy state can react with neutral B to give products A and B^+ . The kinetic processes of interest are:

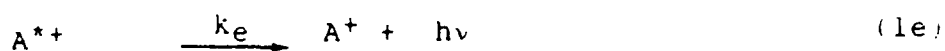
reactive charge transfer,



-nonreactive electronic quenching of A^{*+} by reactant and background neutrals,



radiative relaxation of A^{*+} ,



and back reaction to produce ground state A^+ ion,



We can write for the disappearance of A^{*+}

$$\frac{-d[A^{*+}]}{dt} = (k_a + k_b) [A^{*+}] [B] + k_c [A^{*+}] [A] + k_d [A^{*+}] [M] + k_e [A^{*+}] \quad (2)$$

and for the appearance of B^+ ,

$$\frac{d[B^+]}{dt} = k_a [A^{*+}] [B] - k_f [A] [B^+] \quad (3)$$

For conditions such that $[M] < [A] \ll [B]$ we can rewrite equations 2 and 3 in the approximate forms:

$$\frac{-d[A^{*+}]}{dt} = (k_a + k_b) [A^{*+}] [B] + k_e [A^{*+}] \quad (4)$$

$$\frac{d[B^+]}{dt} = k_a [A^{*+}] [B] \quad (5)$$

Solving equation 4 for $[A^{*+}]$

$$[A^{*+}] = [A^{*+}]_0 \exp[-(k_a + k_b) [B] t - k_e t] \quad (6)$$

where $[A^{*+}]_0$ is the concentration of A^{*+} at $t=0$. Substituting into equation 5 and solving for $[B^+]$ gives:

$$[B^+] = \frac{k_1}{(k_a + k_b) [B] + k_e} [B] [A^{*+}]_0 \left[1 - \exp[-(k_a + k_b) [B] + k_e] t \right] \quad (7)$$

The appearance rate for B^+ can be obtained by plotting $(1 - [B^+]/[B^+]_\infty)$ vs. time where $[B^+]_\infty$ is the final concentration of B^+ . The slope of such a plot is given by

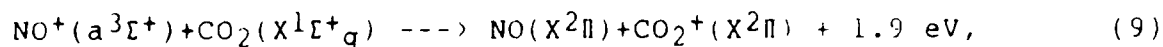
$$m = (k_a + k_b) [B] + k_e \quad (8)$$

A plot of the first order appearance rate of B^+ vs. $[B]$ should have a slope of $k_a + k_b$, the sum of the reaction and quenching rate constants, and an intercept at $[B] = 0$ of k_e , the radiative decay rate. In practice, the $[B]=0$ intercept value reflects the sum of all reactant ion depletion rates which are independent of $[B]$ including such processes as eq. 1-d. Thus the interpretation of this value as a radiative decay rate must be made with careful consideration of the possible contribution of residual gas deactivation. In the studies described here no impurity product ions were observed in the range 10-500 amu, hence any non-radiative process contributing to the reactant ion depletion rate

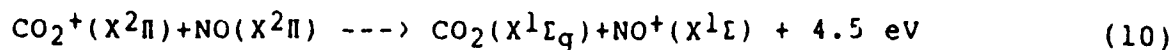
must occur largely through deactivation rather than reaction. This observation aids in assessing the potential contribution of non-radiative processes in the studies described here.

The choice of the probe reactions used in this study is based upon several factors. The rate of the reaction is important since we wish to quickly convert the metastable ion into other species for detection. This minimizes the importance of unreactive quenching collisions. At the same time we require that the neutral be effectively unreactive with the ground state ion. We seek a reaction which produces a single product ion to minimize error associated with product intensity summing. Finally, a reaction is required in which the product ion is relatively unreactive under the conditions employed. That is, we want to minimize back reactions with background NO or O₂ which produce NO⁺(X¹Σ) or O₂⁺(X²Π) and to be free of self-reacting product ions which result in multiple product masses.

Several investigators have studied the kinetics of ion-molecule reactions of NO⁺(a³Σ⁺) and O₂⁺(a⁴Π_u) with neutral partners,^{3,4,30} and their results suggest some suitable probe reactions. The reaction of NO⁺ (a³Σ⁺) with CO₂:

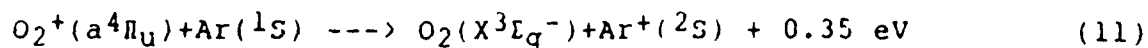


is fast^{4,30} ($k=1.1 \times 10^{-9}$ cm³/sec). The reaction gives solely the charge transfer product (i.e. no electronic quenching). In addition the the back reaction:

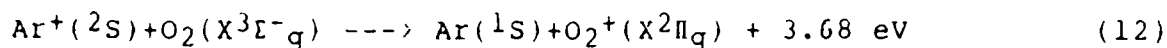


is reported to be slow³¹ ($k=1.2 \times 10^{-10}$ cm³/sec).

The reaction of metastable O_2^+ with Ar:



is also a reasonably fast reaction³ ($k=5 \times 10^{-10}$ cm³/sec) and gives only the charge transfer product. In this case too, the back reaction



is reported to be ten times slower^{32,33} ($k \sim 5 \times 10^{-11}$ cm³/sec).

The reactions, (9) and (11), are used to monitor metastable NO^+ and O_2^+ respectively.

Mixtures of 1% NO in CO_2 and 1% O_2 in Ar were prepared using commercially available gasses with cold trap purification only in the case of NO. No significant impurities were observed in electron impact mass spectra of the mixtures. Experiments were carried out at total pressures of $2-9 \times 10^{-8}$ torr for the NO^+ metastable study and of $1-5 \times 10^{-7}$ torr for the O_2^+ study. Pressures were measured using a Bayard-Alpert type ionization gauge whose readings were corrected for different sensitivities to various gases.

RESULTS

The reactions of $\text{NO}^+(\text{a}^3\Sigma^+)$ with CO_2 and $\text{O}_2^+(\text{a}^4\Pi_u)$ with Ar were studied at ~350 K. Figures 1 and 2 show the energies required to create the respective ionic reactants from the given neutrals.

Preliminary studies of the $\text{NO}^+(\text{a}^3\Sigma^+)$ reaction with CO_2 indicated a long ionic metastable lifetime (small intercept in a first order plot of k vs $[\text{CO}_2]$) and so it was necessary to work under the lowest possible pressure conditions. Reactions were studied over a CO_2 pressure range of from $\sim 2 - 9 \times 10^{-8}$ Torr and with total trapping times at the lowest pressures of up to six seconds.

Data were collected by fixing a total neutral reactant pressure and collecting mass spectra for a range of reaction times. No secondary reaction or impurity products were observed within the detection limits ($<1\%$ of NO^+) over the entire pressure/time range studied. Typical mass spectra are shown in Fig. 4 for $P_{\text{CO}_2} = 5 \times 10^{-8}$ Torr at reaction times of 0, 0.5, and 1.0 seconds. Analysis of the kinetic data collected over a range of CO_2 pressures produced the results shown in Fig. 5 where the first order rates are plotted vs the CO_2 pressure. An unweighted linear least squares fit gives a slope equal to the reaction rate constant of $k = 1.0 \pm 0.2 \times 10^{-9} \text{ cm}^3/\text{sec}$ which is in good agreement with previously determined values^{4,30} of $1.1 \times 10^{-9} \text{ cm}^3/\text{sec}$ and $1.06 \times 10^{-9} \text{ cm}^3/\text{sec}$. (The quoted errors are statistical and do not attempt to evaluate nonrandom errors and are quoted to $\pm 2\%$.)

Table 1

Summary of Experimental Kinetic and Lifetime
Results for $\text{NO}^+(\text{a}^3\Sigma^+)$ and $\text{O}_2^+(\text{a}^4\Pi_u)$

<u>able Ion Reaction</u>	<u>Rate Constant (cm^3/sec)</u>	<u>Metstable Lifetime (sec)</u>
$\text{X}^1\Sigma^+ + \text{CO}_2(\text{X}^1\Sigma) \rightarrow \text{NO}(\text{X}^2\Pi) + \text{CO}_2^+(\text{X}^2\Pi)$	$1.0 (\pm 0.2) \times 10^{-9}$	$1.45 + 1.15$ $- 0.45$
$\Pi_u + \text{Ar}(\text{S}) \rightarrow \text{O}_2(\text{X}^3\Sigma^-) + \text{Ar}^+(\text{S})$	$4.90 (\pm 1.5) \times 10^{-10}$	$0.22 + 0.03$ $- 0.02$

Table AI

Relative Population of Molecular Ionic States Formed by Electron Impact

NO^+		O_2^+	
<u>State</u>	<u>Relative Population</u>	<u>State</u>	<u>Relative Population</u>
$\text{X}^1\Sigma$	15	$\text{X}^2\Pi_g$	34
$\text{a}^3\Sigma^+$	7	$\text{a}^4\Pi_u$	30
$\text{b}^3\Pi$	36	$\text{A}^2\Pi_u$	10
$\left. \begin{array}{l} \text{c}^3\Delta \\ \text{c}^3\Sigma^- \end{array} \right\}$	24	$\text{b}^4\Sigma_g^-$	26
$\text{c}^1\Sigma^-$	<5		
$\text{c}^1\Delta$	<5		
$\text{c}^1\Pi$	18		

deactivation is often quite rapid, even for homonuclear diatomic ions^{61,62}, the neutral O₂ concentration (~1% of total) is low enough to make this effect unimportant.

For these reasons we believe the O₂⁺ state distribution following storage for a period of 50 msec is ~50% O₂⁺(a⁴Π_u, v=0-10) and ~50% O₂⁺(X²Π_g, v=0-10).

O₂⁺

O₂⁺ ions were formed by 70eV electron impact ionization of neutral O₂ and, as in the previous discussion of NO⁺, the initial Franck-Condon determined state distribution may be inferred from the available PES data.^{54,59,60} As indicated in Table AI the O₂⁺ population is divided between the doublet and quartet spin manifolds in approximately equal proportions. The excited doublet states may undergo relaxation via allowed emission to lower lying levels eventually terminating in the ground $2\Pi_g$ state. The lifetime of only one state; $A^2\Pi_u$, $\tau = 670$ nsec, is known, however the other doublet state lifetimes are probably similar.

The only quartet states produced in significant amounts are the lowest $a^4\Pi_u$ state and the $b^4\Sigma^-_g$ state which are formed in approximately equal amounts⁵⁹. The $a^4\Pi_u$ state is formed with a broad vibrational population distribution ($v \sim 0-10$) peaking at $v \sim 5$ while the $b^4\Sigma^-_g$ state appears to be formed mainly in the $v = 0-2$ levels. The $b \rightarrow a$ emission ($\tau \sim 1.1$ μ sec) will, based upon the known emission spectra and Franck-Condon factors²², populate predominantly the $v=0$ and 1 levels of the $a^4\Pi_u$ state. Thus, a fairly broad vibrational distribution peaked at $v = 0$, in the $a^4\Pi_u$ state would be expected to result from the prompt radiative relaxation following ionization. Unlike NO⁺, relaxation of excited vibrational levels in O₂⁺ will be slow since radiative relaxation is forbidden. While charge transfer vibrational

mined by this emission⁵⁵, is 55 nsec. The $W^1\Delta$ and $A^1\Sigma^-$ states are metastable with radiative emission to the $X^1\Sigma^+$ state forbidden by electric dipole selection rules ($\Delta\lambda = 0, \pm 1; \Sigma^+ \leftrightarrow \Sigma^-$). The A' state may decay to the X state via magnetic dipole radiation on a millisecond timescale while the $W^1\Delta$ must decay via quadrupole radiation and thus, in the absence of other effects, may live for seconds.

All of the excited triplets formed may relax by allowed radiative emission. In such fashion, all of the population initially in excited triplet states is funneled into the lowest triplet state, a $^3\Sigma^+$. The timescale for this radiative relaxation has been estimated¹³ to be on the order of 10^{-4} sec. Since the metastable NO^+ is stored in the ICR cell for ~100 msec prior to the initiation of the reaction period (see Experimental Section) it is expected that a significant amount of vibrational relaxation within the $a^3\Sigma^+$ state will also occur. While specific vibrational relaxation rates are not known in this case, it has been suggested⁵⁶⁻⁵⁸ that such rates will be generally faster in ions than in the isoelectronic neutral species.

For these reasons we estimate that the state distribution of NO^+ stored under our experimental conditions for ~100 msec is ~ 2/3 ($a^3\Sigma^+ v=0-2$) and ~ 1/3 ($X^1\Sigma^+ v < 5$), with a possible small amount of $W^1\Delta$.

used in both studies was electron impact, a large number of states are initially formed. Although relatively little is known about the excited electronic states of NO^+ and O_2^+ in comparison with other diatomic molecules, enough is known to draw some conclusions about the final populations of the NO^+ and O_2^+ states existing 100 msec after ionization.

NO^+

NO^+ ions were formed by 70 eV electron impact ionization of NO. At this energy the ionization process is essentially vertical and, to a good approximation, results in final state distributions governed by the Franck-Condon factors connecting the ground state neutral with the various ionic state potential surfaces. The distribution is reflected in the relative peak intensities observed in photoelectron spectra (PES) of NO. The results of several studies⁵⁰⁻⁵⁴ are used to estimate the relative electronic state population of NO^+ produced. The relative populations observed by PES are given in Table AI. As seen in the Table, only one third of the ions produced are in the singlet manifold while one third of the total are formed in the $b^3\Pi$ state. The singlet states formed are the ground $^1\Sigma^+$ state (~15%), and the $A^1\Pi$ state (~18%) along with possible small amounts of the $A^1\Sigma^-$ and $W^1\Delta$ states (see Fig. 1). The $A^1\Pi$ state can radiatively decay to the $W^1\Delta$, $A^1\Sigma^-$ and $X^1\Sigma^+$ states with the frequency factor for emission strongly favoring the latter, giving rise to the Daer-Miescher bands. The lifetime of the $A^1\Pi$ state, as deter-

Conclusions

The lowest electronic spin metastable states of NO^+ and O_2^+ have been studied using FTMS. These states undergo chemical reactions which are distinct from those observed with ground electronic state reactant ions. Under high vacuum conditions ions may be trapped within an ICR cell for long periods of time allowing us to study them under conditions such that the rate of chemical reaction is competitive with the rate of radiative relaxation. The experimental studies allow us to determine the pertinent rate constants for the reaction of the metastable ions with neutral species as well as the lifetime of the reacting ions spin metastable states. The experimental results, summarized in Table 1, show the $\text{NO}^+(\text{a}^3\Pi^+)$ state decays much slower than the $\text{O}_2^+(\text{a}^4\Pi_u)$ state. The forbidden radiative decay mechanism of the NO^+ metastable has been modeled using a four state spin-orbit coupling scheme which provides reasonable agreement with experiment. These studies suggest the potential chemical importance of electronically metastable ions and point out the need for further study of such species.

Appendix

Population of Metastable States

The interpretation of our experimental measurements and theoretical estimates is based upon a knowledge of the metastable electronic states involved and the population distribution of vibrational levels in each. Since the method of ion production

This is in good agreement with the experimentally measured value determined here.

In principle, the same approach could be used to calculate the $O_2^+(a^4\Pi_u)$ lifetime; however, the spread of population over many vibrational levels greatly complicates the situation.

The metastable state lifetimes determined here can be compared with those of isoelectronic neutrals. The lowest metastable quartet state of NO, the $(a^4\Pi)$ level, was studied³⁸ in a matrix of Ne where its emission to the ground $^2\Pi$ state was observed with an apparent lifetime of 156 msec. In separate calculations Lin³⁹ and Lefebure et al.⁴⁰ using theoretical models similar to that used here make lifetime estimates of 130 msec and 100 msec respectively. This system has particular relevance to the present study in light of the electronic similarity of NO and O_2^+ . A theoretical study of CO by James⁴¹ estimated the lifetime of the lowest spin metastable state to be 8.7 msec, in excellent agreement with experimental values of 4.4 msec⁴⁸ and 7.5 msec⁴⁹. While isoelectronic with NO^+ , the ordering of metastable states differs in CO and so no direct comparison is possible. However, the analogous transition in the isoelectronic N_2 molecule has been studied giving a lifetime of $\sim 1.3 - 2.5$ seconds⁹.

$\tau(A^1\Pi) = 55 \text{ nsec}^9$ while the unobserved $b \rightarrow a$ transition is probably much weaker $\tau(b^3\Pi) \sim 140 \mu\text{sec}^{13}$. This fact, and the large energy denominator in the C_2 term suggest the dominant contribution to the $a^3\Sigma^+ \rightarrow X^1\Sigma^+$ transition rate is due to the first term in eq. 17.

The intrinsic rate of decay of the $(a^3\Sigma^+)$ state is⁴³

$$1/\tau = \frac{64 \pi^4 \nu^3}{3 hc^3} \langle a^3\Sigma^+ | er | X^1\Sigma^+ \rangle^2 \quad (18)$$

Neglecting the second term in eq. 17 gives

$$1/\tau = \frac{64 \pi^4 \nu^4}{3 hc^3} C_1^2 \langle A^1\Pi | er | X^1\Sigma^+ \rangle^2 \quad (19)$$

The spin orbit coupling term in eq. 15 has been estimated^{44,45} to be $\sim 19 \text{ cm}^{-1}$. Using the known lifetime of the $A^1\Pi$ state and vertical energies from Edquist et al.⁴⁶ and Albritton et al.¹⁴ we arrive at

$$\begin{aligned} 1/\tau &\approx C_1^2 \left(\frac{\nu_{(3\Sigma - 1\Sigma)}}{\nu_{(1\Pi - 1\Sigma)}} \right)^3 \left(\tau_{1\Pi} \right)^{-1} \\ &\approx \left(\frac{19 \text{ cm}^{-1}}{26,200 \text{ cm}^{-1}} \right)^2 \left(\frac{23500 \text{ cm}^{-1}}{49,700 \text{ cm}^{-1}} \right)^3 \left(55 \times 10^{-9} \right)^{-1} \\ &\approx 1 \text{ sec}^{-1}. \end{aligned} \quad (20)$$

$$|a^3\Sigma^+\rangle = |a^3\Sigma\rangle + C_1 |A^1\Pi\rangle \quad (13)$$

$$|X^1\Sigma^+\rangle = |X^1\Sigma\rangle + C_2 |b^3\Pi\rangle \quad (14)$$

where the coefficients C_1 and C_2 are given by

$$C_1 = \frac{\langle A^1\Pi | H_{SO} | a^3\Sigma \rangle}{E(a^3\Sigma) - E(A^1\Pi)} \quad (15)$$

$$C_2 = \frac{\langle b^3\Pi | H_{SO} | X^1\Sigma \rangle}{E(X^1\Sigma) - E(b^3\Pi)} \quad (16)$$

Calculation of the transition rate for the $(a^3\Sigma^+) \rightarrow (X^1\Sigma^+)$ decay involves the evaluation of

$$\begin{aligned} \langle a^3\Sigma^+ | er | X^1\Sigma^+ \rangle &= C_1 \langle A^1\Pi | er | X^1\Sigma^+ \rangle \\ &+ C_2 \langle a^3\Sigma^+ | er | b^3\Pi \rangle \end{aligned} \quad (17)$$

where er is the electronic transition dipole moment operator. All of the terms in equations 15-17 are known or can be estimated. The A-X transition is known to be strong

consider Fig. 1. The (a-X) transition may occur if either state has both singlet and triplet character. The first order state functions (with primes) can be represented as

$$|a^3\Gamma\rangle' = |a^3\Gamma\rangle + \sum_J \frac{\langle S_J | H_{so} | a^3\Gamma \rangle \cdot |S_J\rangle}{E(a^3\Gamma) - E(S_J)} \quad (11)$$

and

$$|X^1\Gamma\rangle' = |X^1\Gamma\rangle + \sum_K \frac{\langle T_K | H_{so} | X^1\Gamma \rangle \cdot |T_K\rangle}{E(X^1\Gamma) - E(T_K)} \quad (12)$$

S_J and T_K denote the various singlet and triplet states which may mix with the $a^3\Gamma$ and $X^1\Gamma$ states respectively through the spin orbit operator H_{so} . These equations refer only to a single M_S spin component of a given triplet state, however, this distinction will not be made explicit here. In effect, the spin sublevels are assumed to be mixed by collision or rotation.

The energy difference in the denominator of eqs. 11 and 12 suggests that only a single perturbing state need be considered if all others have substantially greater energy defects. Examination of Fig. 1 reveals that the only nearby triplet state which is connected to the ($a^3\Gamma$) state of NO^+ by an allowed electric dipole transition is the ($b^3\Pi$) state. Similarly, the only nearby singlet state which is coupled to the ($X^1\Gamma$) state by an allowed electric dipole transition is the ($A^1\Pi$) state. Thus, we re-write eqs. 11 and 12 as

Theory and Discussion

Both the $\text{NO}^+(\text{a}^3\Sigma^+)$ and $\text{O}_2^+(\text{a}^4\Pi_u)$ states are metastable with respect to the ground electronic states by virtue of spin difference. The prohibition against intercombination transitions between states with different spin is equally valid for all electric and magnetic multipole transitions and so it is usually considered as a dipole transition which gains some allowed character through perturbation of the states involved, specifically the effect of spin-orbit coupling. This coupling is a manifestation of the fact that molecular electronic states are not pure states of a given spin value, but mixtures of such states. Thus, a precise theoretical description of the spin-orbit coupling or the evaluation of a transition strength allowed by such interactions is a laborious task³⁷.

If approached from the standpoint of perturbation theory, several simplifying approximations can be reasonably made which permit the estimation of excited state lifetimes in cases where little detailed spectroscopic data is available. Several variations of this approach have been used to treat similar systems; they differ somewhat in sophistication³⁸⁻⁴². We employ an approach similar to that used by James⁴¹ to calculate the lifetimes of the metastable ions.

In this approximation the transition is considered to occur by mixing one of the participating electronic states with another of the proper spin and symmetry. To see how this approximation can be applied to the calculation of the $\text{NO}^+(\text{a}^3\Sigma^+)$ lifetime,

formed by Penning ionization or that they rapidly relax in the He buffer gas. In the present study a substantial population of excited vibrational levels is expected to result from the electron impact ionization of O_2 (see Appendix). Since infrared radiative vibrational relaxation of such levels is forbidden these states are believed to survive the (50 msec) relaxation period used in the trapping cell. Thus, the agreement of rate constants suggest either an insensitivity of the reaction to vibrational excitation, or the undetected presence of vibrational excitation in the flow tube studies.

As seen in Fig. 6, the zero pressure intercept is $k = 4.55 \pm 0.5 \text{ sec}^{-1}$, (Table I). As a result of the higher reactant pressure employed in this study the effect of deactivation due to residual background gas can be ignored with confidence. The lifetime of the $O_2^+(a^4\Pi_u)$ state determined from the intercept is

$$\tau = 1/k = 0.22 \begin{matrix} + 0.03 \\ - 0.02 \end{matrix} \text{ sec.}$$

As compared to the previous case this transition is less strongly forbidden and might be spectroscopically observable. Comparison with isoelectronic species provides lifetime estimates in good agreement with our measurement as will be seen in the next section.

This radiative rate will be theoretically considered in the next section and comparisons made with corresponding transition rates in isoelectronic molecules. The experimental results are summarized in Table 1.

Preliminary studies of the $O_2^+(a^4\Pi_u)$ charge transfer reaction with Ar demonstrated a substantially faster reaction rate than for $NO^+(a^3\Pi^+)$. For this reason, the studies were performed with Ar pressure of $1 - 5 \times 10^{-7}$ Torr. Reaction rates of $5 - 10 \text{ sec}^{-1}$ were observed making long ion storage times unnecessary. Data were collected in the same way as above and, as before, no impurity or secondary reaction products were observed.

The results of kinetic measurements over a range of neutral Ar reactant pressures are shown in Fig. 6. A linear least squares fit to the data gives a charge transfer reaction rate, $k = 4.9 \pm 1.5 \times 10^{-10} \text{ cm}^3/\text{sec}$. This compares well with the only other kinetic study of this system^{3,30} which reported $k \approx 5 \times 10^{-10} \text{ cm}^3/\text{sec}$. Since the degree of vibrational excitation in the $O_2^+(a^4\Pi_u)$ state is believed to differ substantially in the flow tube and ICR studies the agreement of measured rate constants is somewhat surprising. Lindiger estimated the extent of $O_2^+(a^4\Pi_u)$ vibrational excitation in their reactant studies through the use of probe reactions. The absence in their work of product N_2O^+ and O_3^+ ions which have been reported to arise from the reactions $O_2^+(a^4\Pi_u, v=4) + N_2$ and $O_2^+(a^4\Pi_u, v=5) + O_2$, respectively³⁶ led to the conclusion that either these states were not

This agreement suggests that the population of excited vibrational levels of $\text{NO}^+ (a^3\Sigma^+)$ which are present (see Appendix)³⁴ do not react very differently than the $v=0$ level or that a similar degree of vibrational excitation existed in the previous high pressure studies. A more thorough study of excited vibronic levels is presently underway³⁵.

The zero pressure intercept as determined by the least squares fitting is $k = 0.69 \pm 0.3 \text{ sec}^{-1}$. As discussed above this residual deactivation rate also contains the quenching rate due to background gas. Quenching by either CO_2 or neutral NO does not contribute to the intercept value since the quenching would scale with pressure. Assuming the residual gas (base pressure $< 5 \times 10^{-9}$ Torr) quenching to make a significant contribution to the intercept rate would require a quenching rate constant of $\geq 4 \times 10^{-9} \text{ cm}^3/\text{sec}$. We conclude such processes make $< 10\%$ contribution to the intercept rate. A major constituent of the background gas is N_2 . Which is known⁴ to react with $\text{NO}^+ (a^3\Sigma^+)$ to give the charge transfer N_2^+ product. The N_2^+ product is not observed. It should be emphasized that any contribution reaction I-d makes will lengthen the measured lifetime of the $\text{NO}^+(a^3\Sigma^+)$ state, reported here. With this in mind, we calculate the $\text{NO}^+(a^3\Sigma^+)$ radiative lifetime to be,

$$\tau = 1/k = 1.47 \begin{matrix} + 1.15 \\ - 0.45 \end{matrix} \text{ sec.}$$

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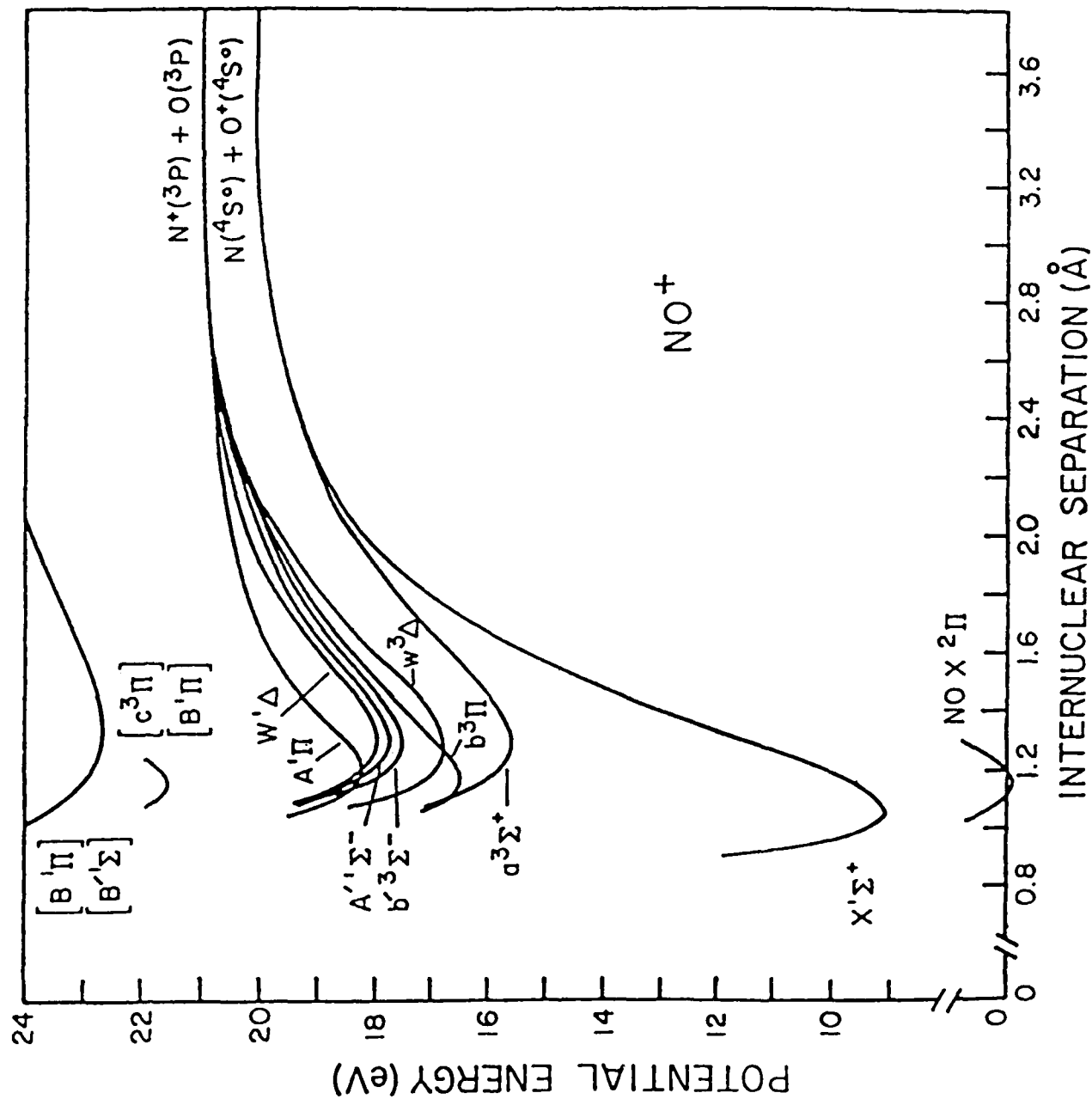
Figure Captions

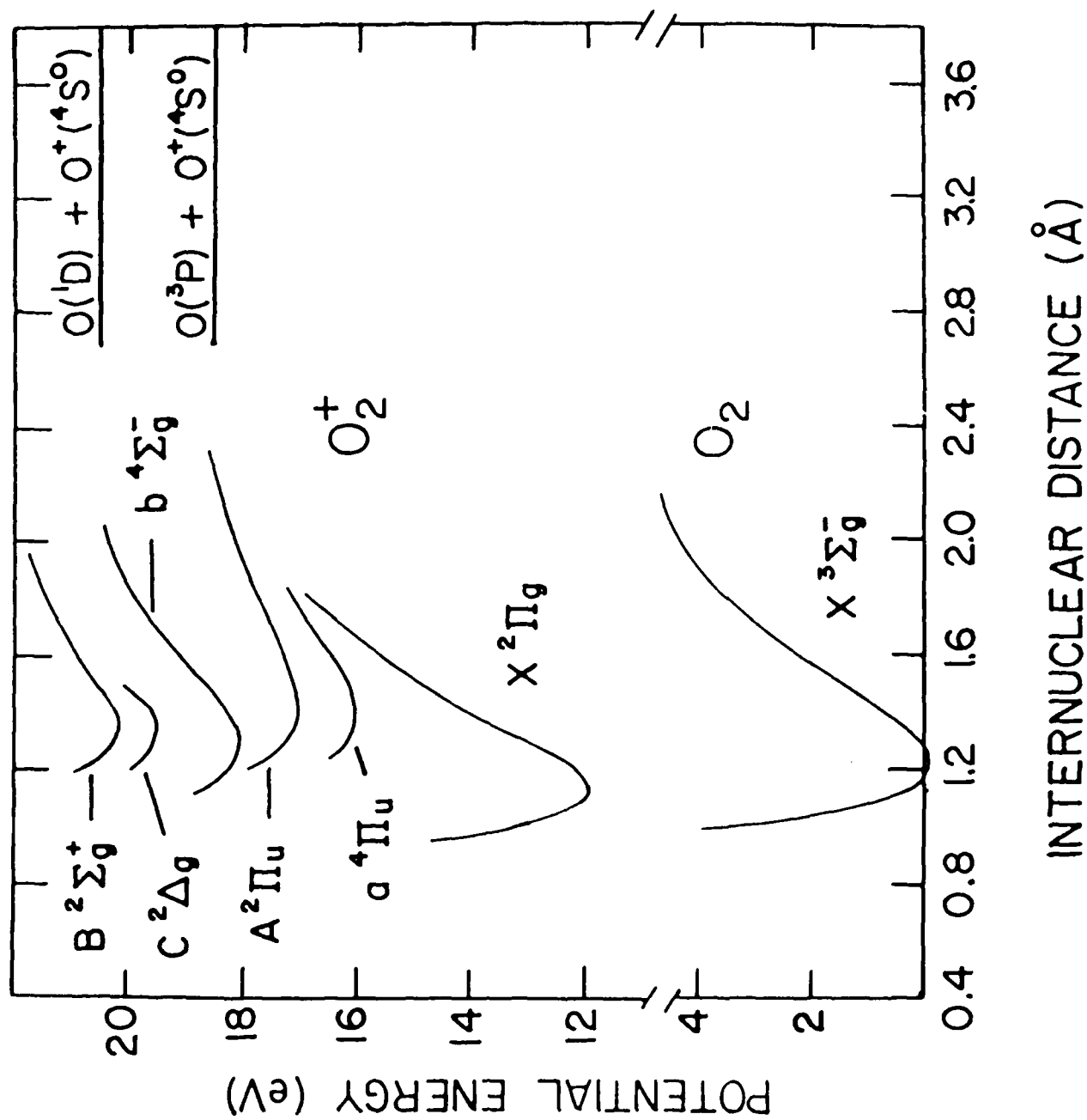
- Fig. 1 Calculated potential energy curves for NO^+ (adapted from Albritton, et al., Ref. 14). Vertical ionization of ground state neutral NO results in a substantial (60% of total) population being formed in the triplet state manifold. This population rapidly relaxes into the ($a^3\Sigma^+$) state from which it reacts.
- Fig. 2 Calculated potential energy curves for O_2^+ (adapted from Krupenie, Ref. 22). Vertical ionization of ground state neutral O_2 results in comparable amounts of doublet and quartet state ions. After a 50 msec relaxation time the metastable quartet population is believed to be spread over a range of vibrational levels within the ($a^4\Pi_u$) state.
- Fig. 3 Typical sequence of experimental events used for the isolation and kinetic study of the NO^+ metastable state ion. The sequence of events in the study of the O_2^+ metastable state ion is the same although the relaxation times and ejection frequencies are changed.
- Fig. 4 Typical data for the reaction of metastable state NO^+ with CO_2 at a CO_2 pressure of 5×10^{-8} torr. Reaction times in a, b, and c are 0.0 sec, 0.5 sec., and 1.0

sec. respectively. The absence of impurity products such as N_2^+ or H_2O^+ suggests that collisional quenching of the reactant excited state ion is not a major loss mechanism.

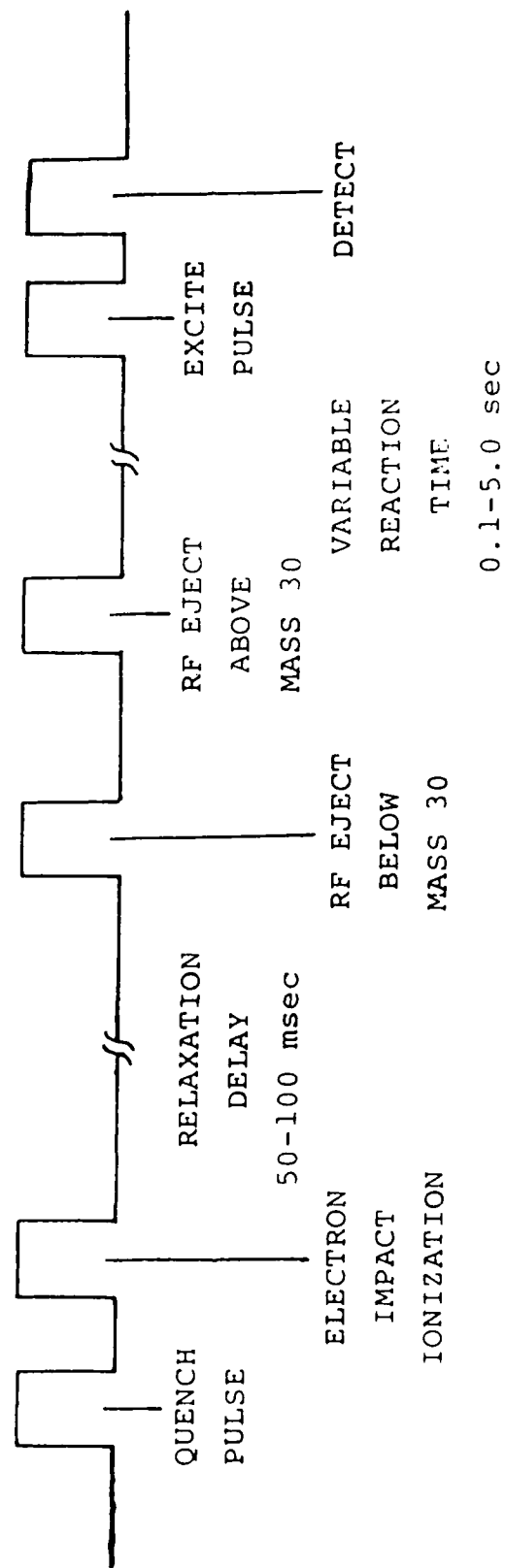
Fig. 5 Appearance rates for CO_2^+ from the reaction of metastable electronic NO^+ with CO_2 vs CO_2 pressure. The slope of the plot equals the charge transfer reaction rate constant, $k_{ct} = 1.0 \pm 0.2 \times 10^{-9} \text{ cm}^3/\text{sec}$. The zero pressure intercept, $k = 0.69 \text{ sec}^{-1}$, equals the sum of all deactivation processes which are independent of CO_2 and NO pressure and sets a lower limit (see text) of 1.45 sec. for the radiative lifetime.

Fig. 6 Appearance rates for Ar^+ produced by the reaction of electronic metastable O_2^+ with Ar vs Ar pressure. The slope determines the charge transfer rate constant, $k_{ct} = 4.9 \pm 1.5 \times 10^{-10} \text{ cm}^3/\text{sec}$. The zero pressure intercept of 4.55 sec^{-1} provides a lower limit to the $O_2^+(a^4\Pi)$ state lifetime of 0.22 sec.

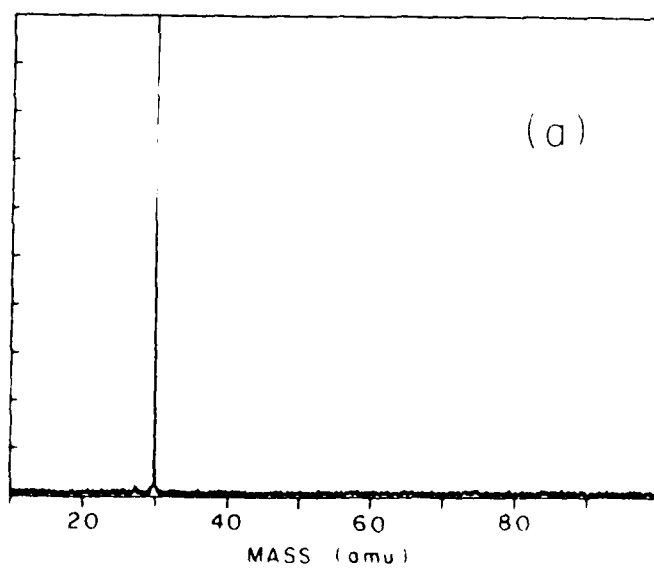
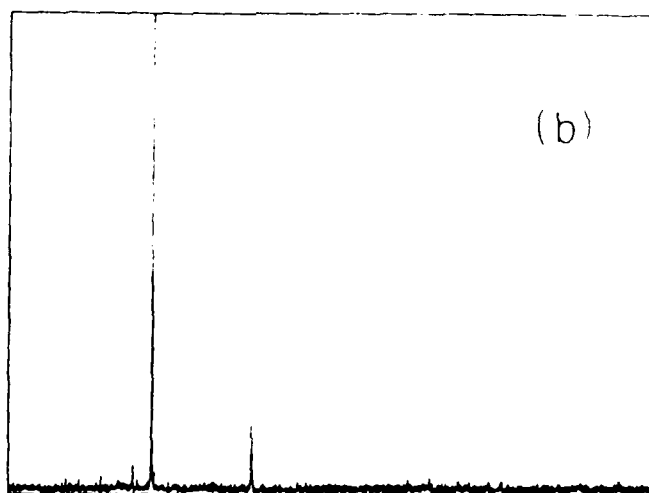
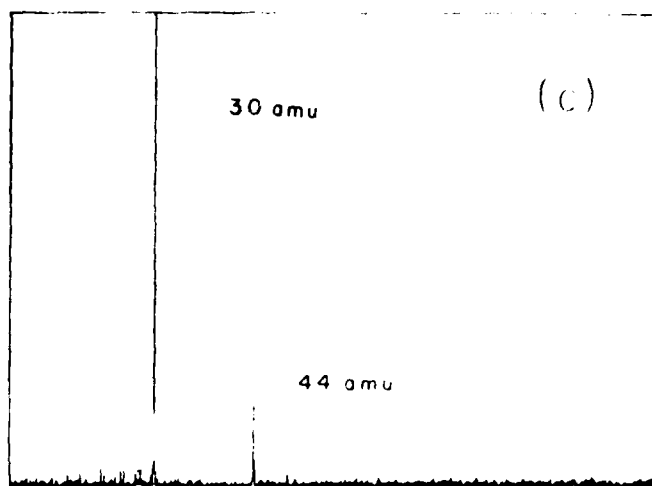


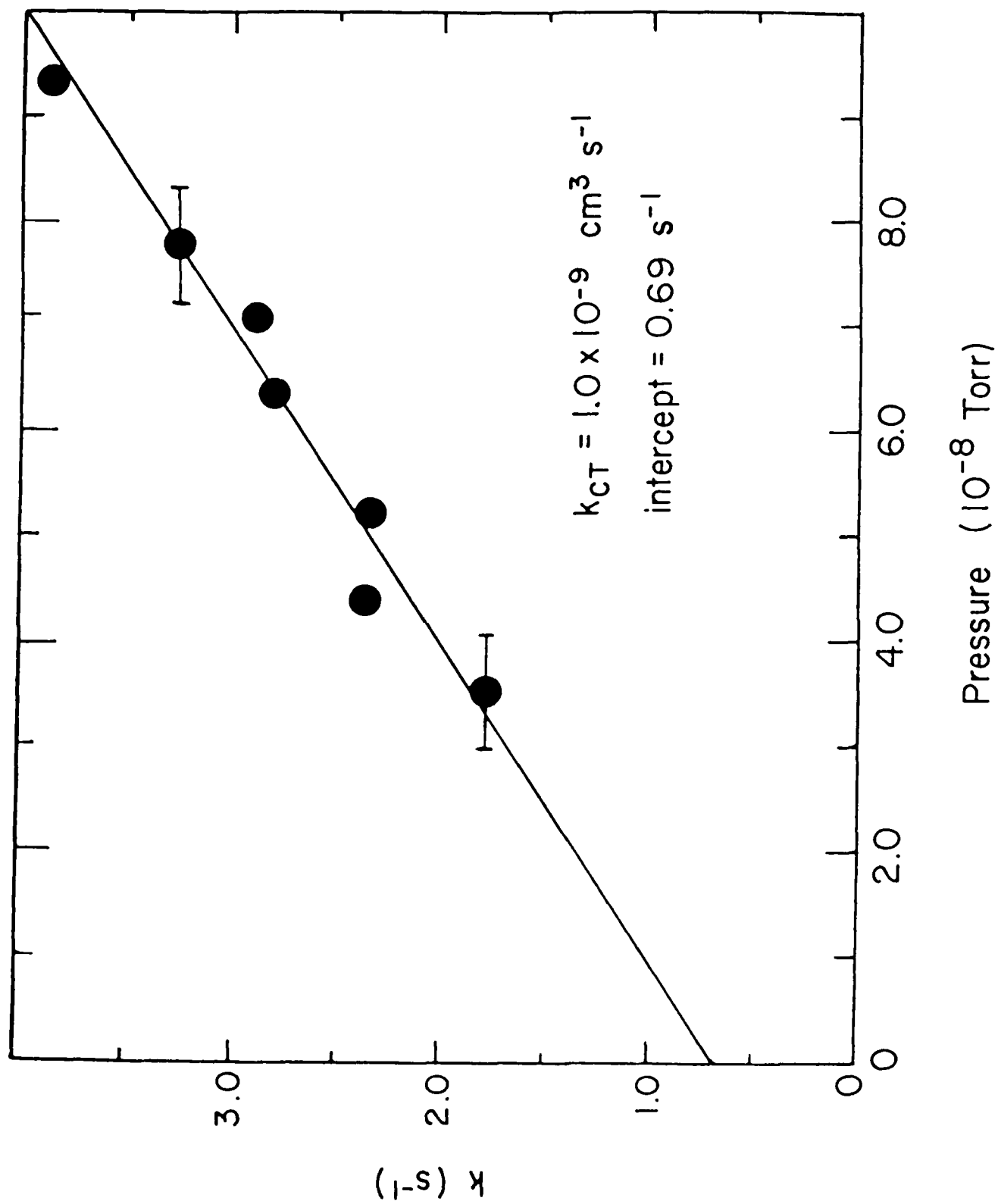


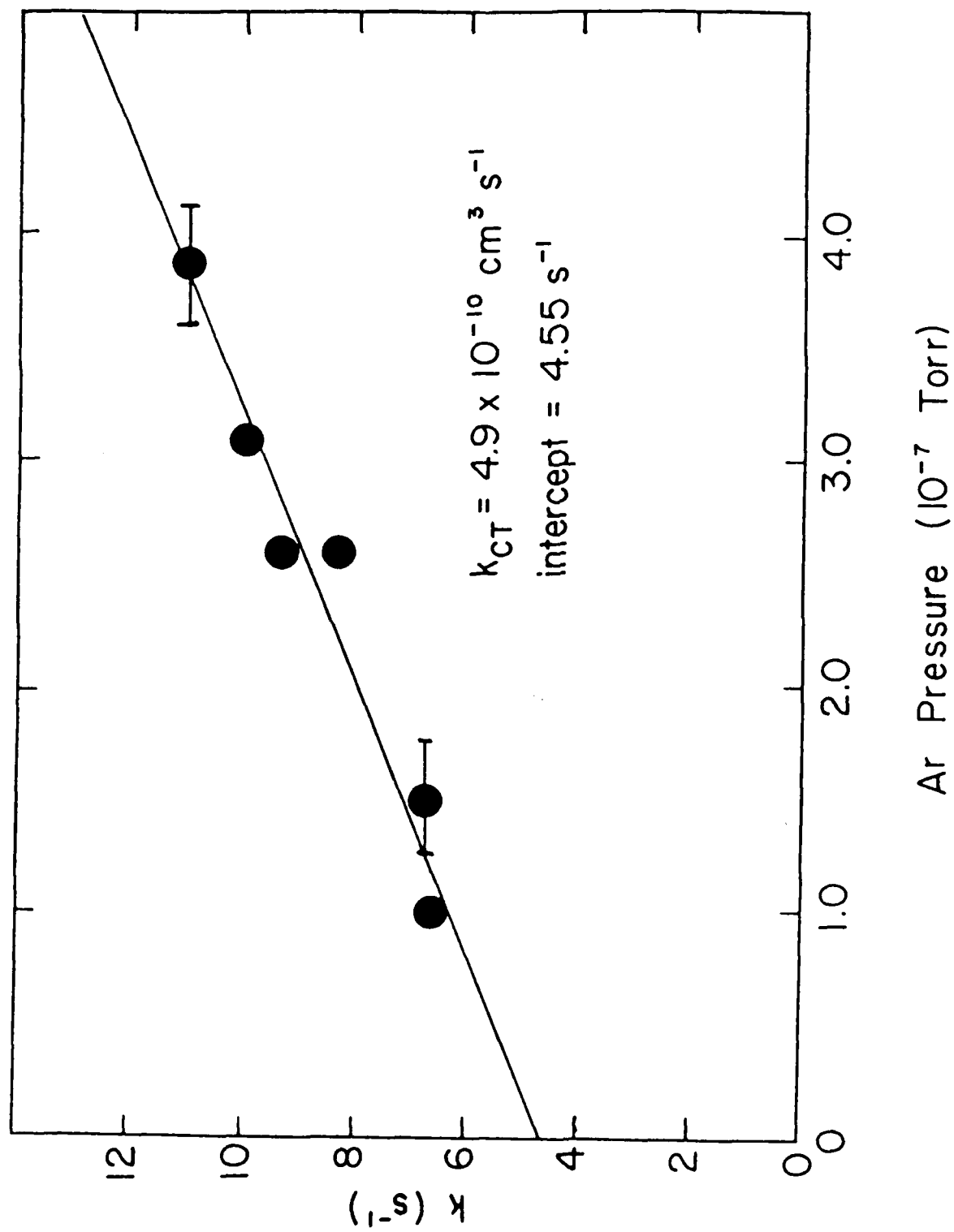
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